Shape Control of Bimetallic Nanocrystals

As reported in *Nature Materials*, Peidong Yang and Gabor Somorjai have developed a new method for producing bimetallic nanocrystals with controlled shapes through the overgrowth of one metal on the cubic seeds of another metal. Large cubes, cubo-octahedra, octahedra, and rods were obtained.

The physical and chemical properties of nanocrystals are highly shape dependent, but although some techniques exist for making certain shapes for some compositions, a general methodology for achieving morphological control during nanocrystal synthesis, for both single- and multiple-material systems, has remained empirical and challenging.

The LBNL team began with a known system for which size and shape control had been achieved: cubic platinum (Pt) nanocrystals. They then used the Pt nanocrystals as seeds for the overgrowth of a second metal under solution-phase conditions that were designed to control nucleation and growth of the second structure. In doing so, they were guided by principles which have been developed for gas-phase "heteroepitaxy" (growth of one crystal on top of another), which is used widely to produce functional heterostructures for devices such as integrated circuits and solid-state lasers.

First, the team overgrew Pd, with has a lattice constant similar to that of Pt, on the cubic Pt "core" seeds. Reduction of an aqueous Pd precursor under standard conditions yielded larger core-shell nanocrystals with the same cubic shape. Next, they added nitrogen dioxide (NO_2), which is known to interact with the Pd surface. By varying the amount of NO_2, the relative rates of the growth of different Pd facets could be controlled. By increasing the NO_2 concentration, first cubo-octahedra and, then octahedral bimetallic nanocrystals with >90% shape selection were produced. Finally, they switched the overgrowth metal to gold (Au), which has a larger lattice constant than Pt. In this case, when the Au precursor was reduced in the presence of the Pt seeds, the overgrowth was not conformal. Instead, rod-shaped nanocrystals were produced, minimizing the build-up of strain energy due to the lattice mismatch. The catalytic activity of the various Pt/Pd bimetallic nanocrystals was evaluated by studying the electrochemical oxidation of formic acid. The cubic crystals had a oxidation rate five times higher than the octahedral crystals, with the properties of the cubo-octahedral crystals falling in between.

The work demonstrates that by controlling the epitaxial overgrowth of a secondary metal on well-faceted seeds, both conformal shape-controlled overgrowth as well as anisotropic overgrowth can be produced, depending on the degree of lattice mismatch. This concept could be applied to other material systems (for example, Rh, FePt and CoPt), creating novel heterostructures with controlled catalytic, optical, and magnetic properties.

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